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GRADIENT POLYMERS(U) CALIFORNIA UNIV BERKELEY DEPT OF  
CHEMICAL ENGINEERING M C WILLIAMS ET AL. 31 AUG 84  
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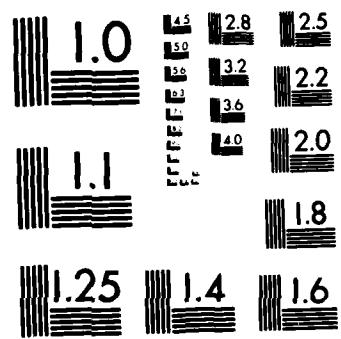
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DEPARTMENT OF CHEMICAL ENGINEERING  
BERKELEY, CALIFORNIA 94720

September 3, 1984

Dr. Kenneth J. Wynne  
Office of Naval Research  
Scientific Officer - Code 413  
800 N. Quincy  
Arlington, VA 22217

Re: Contract N00014-  
75-C-0955  
(Final Report)

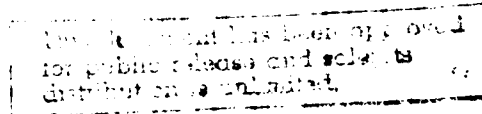
Dear Dr. Wynne:

This contract terminated on August 31, 1983. In a letter dated December 15, 1983, Mr. David R. Van Metre (ONR contracting officer) denied my request for an extension--all ONR funds had been consumed--but agreed to wait until August 31, 1984 for the final report.

In complying with the spirit of that agreement, I am submitting here-with a preliminary version of the final report. In earlier correspondence I explained the difficulties I was having with the student, whose thesis will constitute the final report. She is currently working very well and I expect her to complete the thesis by December 1984 (roughly the time scale I projected for ONR last November).

No data beyond that which is contained in this preliminary report is currently in my hands. However, a very large amount of data will be in the Ph.D. thesis. I am sure we will all be pleased with that final result. Thank you for your patience.

Sincerely,



*Michael C. Williams*

Michael C. Williams  
Professor

MCW/ds  
encl. - report (1)

cc: ONR Branch Office, Pasadena (1)  
Mr. Cristal C. Grisham, ONR  
Administrative Contracting Officer (1)  
Naval Research Laboratory (6)  
ONR Code 102IP (6)  
Defense Documentation Center (12) —

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Preliminary  
FINAL TECHNICAL REPORT

GRADIENT POLYMERS

ONR CONTRACT N00014-75-C-0955

Principal Investigator:

Research Assistant:

Institution:

Administering Department:

Period:

Prof. M.C. Williams\*

Ms. Jeanne E. Stoughton

University of California, Berkeley  
Berkeley, CA 94720

Chemical Engineering

March 1, 1975 through a succession of  
extension dates to August 31, 1983

August 31, 1984

Prepared for the Office of Naval Research



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\*Replacing Prof. Mitchel Shen, upon Shen's demise in August 1979.

## GRADIENT POLYMERS

### INTRODUCTION

Gradient polymers represent a unique type of polymer blend, consisting of two chemically-different chains which are forced to intermingle despite thermodynamic forces that act in the direction of phase separation. They are prepared by first fabricating a crosslinked host polymer, then causing a foreign monomer to diffuse into the host, and finally polymerizing and crosslinking the penetrant in situ. In the limiting case of host saturation (i.e., a uniform distribution of the penetrant), the resulting blend is called an "interpenetrating network" (IPN); this name is not fully descriptive of the penetrant uniformity, but was adopted years ago when the IPN was the only variant being studied. *This paper discusses studies on* ~~In our work, we studied the more general case of~~ nonuniform and nonequilibrium penetrant distributions, wherein a gradient of the second polymer is ~~frozen~~ *it is expected* in place by the crosslinking reaction. In a general sense, ~~we expect~~ that ultimately a wide range of physical properties--possibly some quite unique--will arise from controlling not only the choice of the two polymer species but also the composition gradient.

The early years of this project, under the direction of Prof. Mitchel Shen, led to three publications<sup>1-3</sup> that will not be reviewed here. Suffice it to say that these papers remain almost alone in the field, in part because the task of preparing gradient polymers is so difficult. Perhaps for this reason, there were many questions raised about the earlier work,<sup>1,2</sup> and some of those results<sup>2</sup> could not be reproduced.<sup>3</sup> Thus, the focus of the work since 1979 (directed by Prof. Michael C. Williams) was to select one new chemical system, develop reproducible methods of sample preparation, invoke new analytical

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techniques for sample characterization, and conduct mechanical property tests of great variety (linear and nonlinear).

The chemical system ultimately selected was a crosslinked polymethylmethacrylate (PMMA) host that was penetrated by a low-molecular-weight grade of polybutadiene (PB), subsequently to be further polymerized and crosslinked in its gradient position. Such a choice necessarily limits the scope of the present study to represent variations of only one class of material: the two-component rubber-toughened plastic. However, this is a very important class of structural plastic, and the possible compositional variations are highly diverse in principle.

Primary results consist of the measured responses to various types of mechanical deformation, including ultimate limits. These are coupled with information about the chemical composition (averages, and gradient character) and the microstructure to develop correlations and predictive rules for material performance. The present preliminary report does not include all of these results, but the final version of the report will do so.

#### SAMPLE PREPARATION

Roughly 80% of the time and effort on this project (i.e., the first four years, 1979-83) has been devoted to optimization of the PMMA/PB preparational variables and implementation of characterization methods. These phases of the work can be described with some completeness, though a full recitation of details will await the final version of this report.

##### A. Host Polymer

The hard plastic host was chosen to be PMMA, lightly crosslinked, which is inexpensive and is easily machined into specimens for mechanical testing. It was polymerized here and machined in the UCB College of Chemistry shops, so that its composition and history were entirely known to us.

The mixture of monomer (MMA) plus azo-bis-isobutyronitrile (AIBN) initiator plus ethylene glycol dimethacrylate (EGDMA) crosslinker was degassed twice, to reduce subsequent irregularities such as bubble formation and shrinkage; omission of this step initially caused so many imperfections in the specimens that very few were suitable for testing. Polymerization was conducted in ordinary fluorescent lighting. The reaction rate was kept slow by using very little AIBN, and 48 hours was needed to approach completion. The resulting PMMA was then crosslinked in a vacuum oven at 130°C for two days and slowly cooled to room temperature over a 24-hour period; substantial annealing also occurred during this treatment. The choice of 130°C was dictated by the activation of the crosslinker, but it also proved to be high enough to ensure chain mobility (note,  $T_g$  for PMMA ranges from 105° for uncrosslinked samples to no more than 115° for the crosslinked samples used here) and this permitted virtual completion of all reactions; only a trace of unreacted MMA has been detected in the final material.

The rough cylindrical samples -- having been produced in cylindrical ampules -- were next machined on a lathe to either a symmetrical dumbbell shape or a perfect cylinder, suitable for subsequent tensile or torsional testing. Meticulous polishing of the surface was conducted with a sequence of agents, from fine emery paper through several grades of alumina (to 0.05  $\mu$ ), and thus surface imperfections which often distort the results of mechanical tests were removed. Examination of samples under polarized light showed no residual anisotropic strains due to production or processing steps to this point.

#### B. Penetrant Phase

The penetrant molecule was required to be one which forms a rubbery polymer at room temperature, so that the full range of physical states (glassy

to rubbery) in the blend could (in principle) be explored. However, this basic contrast of properties was itself a source of numerous obstacles: even small molecules do not generally penetrate well into glasses, and diene hydrocarbons (most monomers for rubbers) are usually incompatible -- i.e., of marginal solubility -- in polar compounds such as methacrylates. All these problems were eventually surmounted.

(1) Selection of penetrant. Testing of numerous unsaturated monomer types verified their lack of compatibility with the host plastic; contact of these pure liquids with PMMA caused very little swelling of the latter at room temperature. Working at higher temperature to soften the host was not possible because the candidate monomers were too volatile. However, a low-molecular-weight ( $\bar{M} = 1050$ ) prepolymer of polybutadiene (PB) was obtained from Polysciences (Warren, PA) and found to remain stable as a viscous liquid even at 130°C. This PB was thus chosen as the penetrant, with the expectation that a coiled chain molecule of  $\bar{M} = 1050$  would still be small enough to diffuse into the matrix of another rubber (PMMA at 130°C is in the rubbery state). Information provided by Polysciences included the  $\bar{M}$  and the chain isomeric structure: 85% vinyl (1,2 linkage) with the remaining 15% (1,4 linkage) mostly in the cis state.

(2) Polymerization considerations. Several initiator schemes for extended polymerization of the PB prepolymer were examined: AIBN with UV light, benzoyl sec-butyl ether with UV light, ammonium persulfate with UV light, benzoyl peroxide with heat, AIBN with heat, and dicumyl peroxide (DCP) with heat. No appreciable polymerization took place with the UV schemes and these were discarded. The thermal methods were more successful, and DCP was selected because a great deal of information on its behavior in such systems is available.



Since the gradient samples were to be produced by diffusion of PB into PMMA at 130°C, it was important to examine also the rubber stability at this temperature. Only a slight degree of yellowing was observed even in the bulk rubber after exposure to 130°C for four days. However, it was deemed prudent to add an anti-oxidant stabilizer -- butylhydroxy tin (BHT) -- to eliminate all such problems during sample preparation, storage, and testing.

Preliminary tests made by polymerizing the PB prepolymer mixture alone showed that the resultant rubber was not of optimal quality when DCP was the only initiator/crosslinker. Addition of EGDMA (used also in the PMMA crosslinking) led to superior rubber properties. Thus, for preparing the gradient samples, both DCP and EGDMA were used in the prepolymer mixture.

Diffusion enhancement. Preliminary trials with the prepolymer PB containing 1% DCP showed that penetration into the host PMMA at 130°C was negligible in the time available before the rubber polymerized. The PMMA cylinders appeared to be unmodified, and even at their surfaces no softened areas were observed. In view of possible free volume limitations in the host, even though  $T > T_g$ , it was decided to produce additional swelling with a solvent reasonable good for both PMMA and PB. Experiments at room temperature were conducted with p-xylene, toluene, cyclohexanone and tetrahydrofuran. All except p-xylene were eliminated; toluene caused cracking of PMMA, and the others were not sufficiently good solvents for both polymers. P-xylene, which boils at 135°C, caused no PMMA cracking or crazing even at 130°C; samples remained visibly clear, yet swelled to approximately double their original volume within 48 hours. Such samples were highly plasticized and rubbery when removed from the refluxing (sealed) glass ampules.

Although p-xylene (pX) was successful in producing PMMA swelling, it was not initially clear whether the pretreatment of the host cylinder in a

solution of pX and PB (with additives) would have the desired effect while maintaining simplicity of operation. A number of trials of such an operation were conducted, and one sequence is described below.

The base mixture of PB plus 1% DCP was diluted with pX to prepare three solutions: 80%, 70%, and 50% PB by weight. These solutions were used in the role of penetrants for PMMA, and the now-standard procedures led to three samples of gradient polymers. Staining sample cross-sections with bromine (see below) for 2 hours showed significant PB penetration, by the intensity of brownish color across the cylindrical cross-section. The samples prepared from 80% PB and 70% PB had "skins" (dark and light brown, respectively) of high PB concentration near the surface, with clear uncolored centers, while the sample prepared from 50% PB was hazy and yellow throughout. Thus, the pX content of the PB solutions can be manipulated as an extra degree of freedom in controlling the ultimate PB distribution in the blend.

However, visual inspection of various samples suggested that the gradual composition profiles characteristic of Fickian diffusion may be unattainable with these systems. Penetration of the PB appeared to take place behind a sharp front, leading to a two-step region of compositions (or, as the only alternative, the uniform IPN case). This occurred also when samples were prepared from PMMA hosts which had been preswollen with pure pX and thus had more than ample free volume. The preswelling did, however, facilitate the extent of PB penetration, as shown by much thicker "collars" of PB-rich regions when using solutions of 80% PB and 70% PB.

This latter observation, together with the result that using a host PMMA preswollen with pX gave more reproducible samples, led ultimately to adoption of such a technique. Samples designed for mechanical property testing were subsequently made by infusing a pX-swollen PMMA host with three PB prepolymer solutions in pX: 85% PB, 80% PB, and 70% PB; this superficially small range

of composition corresponded to dramatic variation of the prepolymer solution viscosity and hence diffusivity. The penetration, polymerization, and crosslinking process was continued for 18 hours, under vacuum, at 120°C.

#### COMPOSITION ANALYSIS

Use of an unsaturated penetrant (PB) in PMMA made possible the composition profile determination by staining agents that adhere to (or react with) the C=C bond. The most common stain, osmium tetroxide, was rejected for reasons of toxicity and also because it tends to rigidify the rubber and thus prevent its own further penetration. Bromine, while a less intense stain, reacts quantitatively with the C=C bond and gives far less severe problems than OsO<sub>4</sub> in other ways. Thus, our choice was to employ bromine.

Visual inspection of bromine-stained samples permitted a convenient and immediate assessment of gradient polymer composition, albeit a qualitative one (see above). However, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were combined in a more-detailed method of analysis. First, cross-sections of the gradient samples (plus pure PMMA and pure PB) were cut, highly polished by standard methods, and exposed to bromine vapor for 2 hours at room temperature. Next, the brominated samples were placed in the SEM at Lawrence Berkeley Laboratory's Molecular and Materials Research Division, and EDAX was used to count the local density of the bromine K $\alpha$  peaks.

Examples of these results are given in Figs. 1-3. Other tests, using this technique, confirmed that sample preparation methods were capable of reproducing composition profiles with a high degree of success. It should be noted that these profiles were unlike those predicted by Fickian diffusion kinetics, despite the fact that only amorphous materials and a common solvent

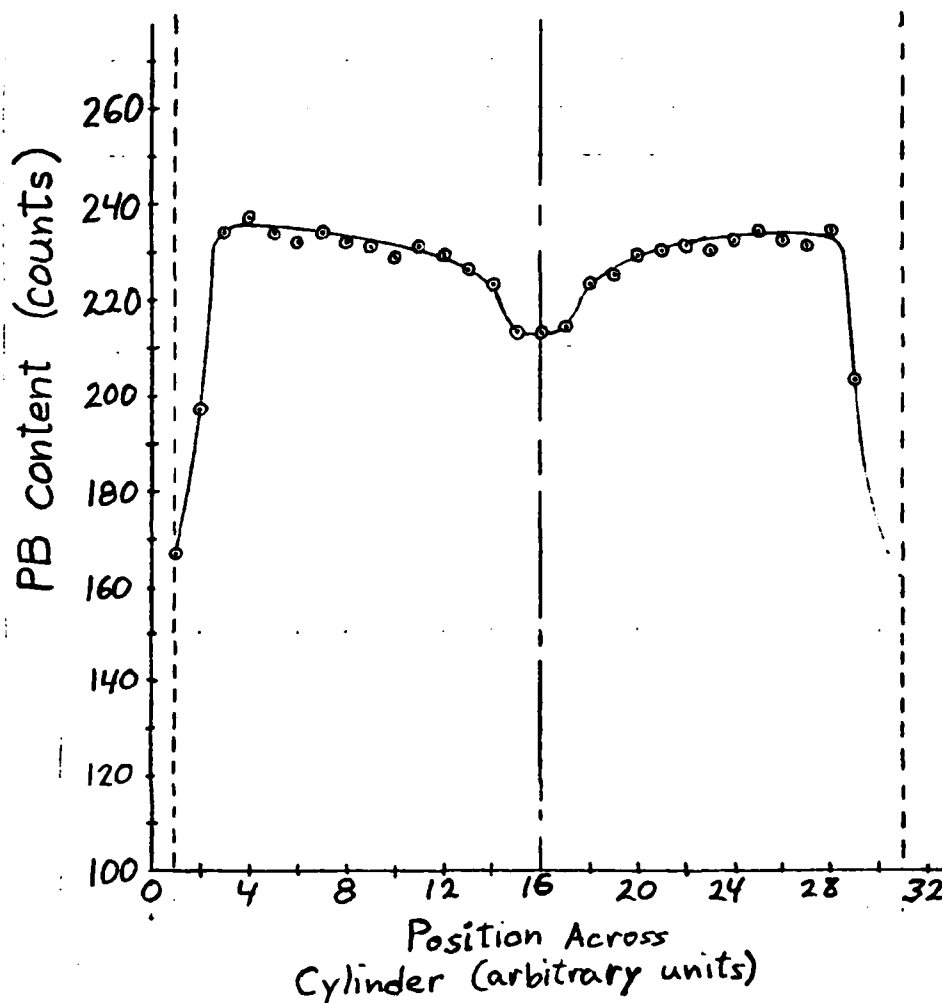


Fig. 1. EDAX measurement of PB concentrations in PMMA across a cylindrical specimen, prepared by immersion of swollen PMMA in a 70% PB solution. Pure PMMA gives 100 counts, so the level of the horizontal axis represents 0% PB. Pure PB gives 2,263 counts (off scale). In this specimen, PB is seen to penetrate into all parts of the cylinder. Composition across the central 80% is nearly uniform; only in a small inner core is there a minor PB deficit. The drop-off at the outer surface is not completely understood and may be an artifact of the sample manipulation in the SEM.

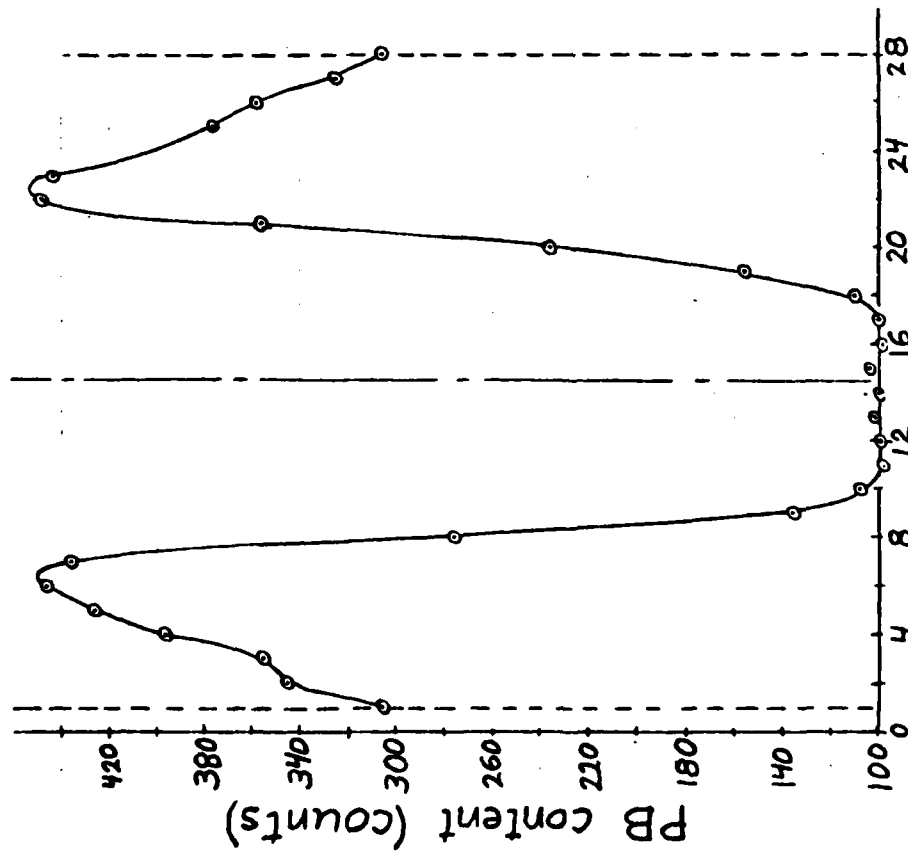


Fig. 2. EDAX measurement of PB composition profile in a specimen prepared using an 80% PB solution. (Note change of vertical scale, relative to Fig. 1.)

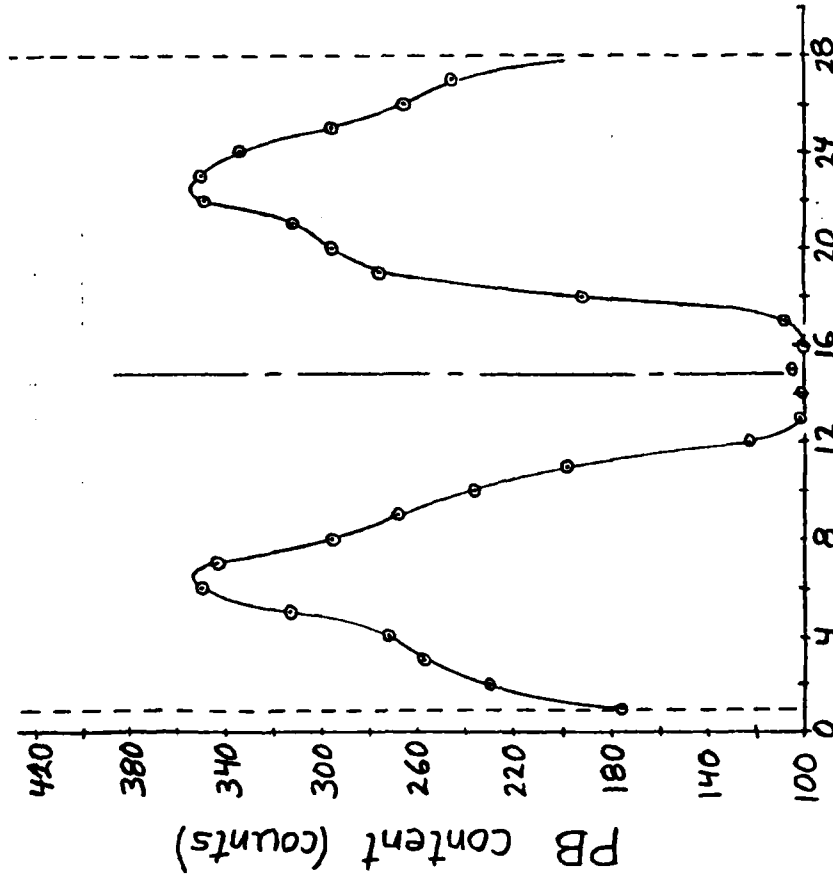


Fig. 3. EDAX measurement of PB composition profile in a specimen prepared using an 85% PB solution. (Same vertical scale as in Fig. 2.)

were involved. There was always a relatively sharp boundary between the advancing PB penetrant front and the soft plastic core. Samples prepared with the 70% PB solution (lowest viscosity) had profiles closest to being uniform --e.g., Fig. 1--and thus were very similar to an IPN. On the other hand, use of the 80% PB and 85% PB solutions always produced the steeply peaked patterns of Figs. 2 and 3, with virtually no PB reaching the PMMA core.

#### MECHANICAL PROPERTIES

Two principal devices-- the MTS Tester and the torsion pendulum--were used to obtain a wide range of linear and nonlinear mechanical properties for the specimens whose compositions were characterized as described above. Ultimately, the correlation between composition and properties will be made, which is the objective of this project; the final version of this report will deal extensively with this problem.

##### MTS Tester

A variety of static and dynamic polymer properties can be obtained, all in a tensile mode, by appropriate programming of the time-dependent strains being imposed in the MTS. In this study, we measured the ordinary "static" stress-strain relationship (thus providing the low-strain modulus and several ultimate properties, such as tensile strength, ductility, and toughness), slow cycling stress-strain (giving hysteresis and insight about internal repair), and fatigue properties. Fracture surfaces were also observed by SEM to assess failure mechanisms.

Initially, Ms. Stoughton received expert training on use of the MTS by spending a week at the General Electric Co. Corporate Research Laboratory (Schenectady, NY) working with Dr. Albert Yee. She subsequently made a detailed evaluation of our MTS and several modifications were introduced:

- (1) Two types of grips were obtained to accommodate small cylindrical samples. One set was ridged and wedge-shaped (especially suitable for materials of rubbery texture), while the other resembled drill chucks.
- (2) Load cell capability was made more sensitive by scaling down from 5000 to 1000 lb.
- (3) Vibrations which interfered with stress measurement at high strain rates (in fatigue tests and others) were eliminated by developing a special damping segment for insertion into the load train.
- (4) Certain machine transients upon start-up were minimized. Design of a novel "slack grip" allowed a specified speed to be reached before the sample was subjected to any stress, thus avoiding problems related to machine inertia.

In addition, to obtain data on sample dimensional and volumetric changes during tensile testing (thus providing insight on failure mechanisms such as crazing), a sensitive diametral extensometer was purchased.

Tensile stress-strain measurements were performed on about 80 samples (2-5 replicates of each type of test on each type of sample). The range of elongational strain rates was  $10^{-4}$  to  $10^{-1} \text{ sec}^{-1}$ , to assess strain-rate sensitivity variations among the different samples. From these curves were determined the low-strain elastic modulus, toughness, overall curve shape, and the stress and elongation at break. Our preliminary evaluation suggests that these characteristics, when averaged among the replicate tests, reveal few differences from the pure PMMA. However, several samples made with 80% PB solutions achieved distinct improvement in toughness at the lowest strain rate. In addition, samples made with 70% PB solutions appeared to be more highly plasticized and to reach greater elongations at a lower stress level.

The lowest-strain-rate tensile tests were also monitored by two strain gauges, reading axial and diametral strain, in an attempt to determine the percent of volumetric deformation taking place before extensive necking in each sample type. Since crazing leads to a high increase in void volume, it was hoped that this could be related to the observations of fracture surface phenomena (exhibition of the characteristic markings of either shear or crazing mechanisms for energy dispersion). Significant differences in volumetric deformation were observed among the sample types, and these will subsequently be discussed in terms of various possible interpretations involving the measured composition profiles and overall rubber content.

Fracture surface morphologies were examined from low to high SEM magnification for each of the four strain rates. This was the most conclusive evidence that the gradient types were quite different in their deformation response. They exhibited different proportions of shear steps, large and small cracks of varied shape, number of bifurcations, and implied crack propagation speeds related to the strain rates at which the tests were run.

Fatigue tests were conducted on a limited number of samples in tension-compression load control. The results appeared to indicate a trend towards softening and weakening the fatigue resistance of the polymer by inclusion of the PB rubber. The homopolymer PMMA gave the largest number of cycles to failure, with the lowest fatigue cycles to failure given by samples made with the 70% PB solutions. We conclude that a hypothetical mechanism by which the PB rubber might have enhanced fatigue resistance by filling in surface cracks or flaws was not operative here.

#### B. Torsion Pendulum (TP)

Our TP, built here and used with reasonable success in several earlier projects, provided the elastic and storage moduli ( $G'$  and  $G''$ ) over temperature



ranges of hundreds of degrees. This linear data in shear supplemented the nonlinear data in tension, obtained with the MTS, and moreover was used as a diagnostic of phase mixing and thermal transitions in polymer samples by what is known as "dynamic mechanical spectroscopy".

The TP operates by free angular oscillation in a torsional mode. A small shear strain is initially imposed on the sample by twisting the heavy "inertial assembly" which grips the specimen end. Releasing the assembly permits free oscillation of decreasing amplitude, until motion is entirely damped out by energy dissipation in the polymer sample. Tracings of the decaying oscillations are derived from an optical transducer system whose accuracy is vital for data analysis, and this system received substantial upgrading:

- (1) The previous light source was a tungsten filament that produced a spectrum similar to the room lighting, so that various forms of interference were common. This was replaced with a GaAs infrared emitter and band pass interference filter.
- (2) Angular motion is measured by the intensity of light transmitted between crossed polarizers, one of which rotates with the sample while the other is stationary. The previous polarizers were made of plastic, were not entirely uniform, and developed warpage which caused random errors from run to run; moreover, they were not suitable for the new IR light source. New glass-laminated Polaroid HR infrared polarizers were obtained and installed.
- (3) A much-improved IR photodetector assembly was installed.
- (4) On-line data analysis was added through coupling to a PET computer, with both analog and digital capabilities. This improved speed and accuracy of obtaining the  $G'(T)$  and  $G''(T)$  spectra from the raw data.

One result of TP testing was identification of the sample glass transition temperatures,  $T_g$  (by peaks in the  $G''(T)$  spectrum). For the pure unswollen PMMA,  $T_g = 120^\circ\text{C}$  was found. Such a value is typical of high- $M$  and crosslinked PMMA. Addition of the pX solvent plasticized the PMMA considerably, lowering  $T_g$  to about  $69^\circ\text{C}$ . Gradient polymers produced with 85% PB and 80% PB solutions (i.e., 15% and 20% showed even greater plasticization, with  $T_g \approx 51^\circ\text{C}$ ; this was surprising in view of the chemical evidence (Figs. 2 and 3) that no PB penetrated into the PMMA core, so the implication is that more pX reached the core--ahead of the PB front--than when pX alone was diffusing. The result that samples made from 70% PB solutions lowered  $T_g$  still further, to about  $47^\circ\text{C}$ , continued this progression but was less surprising since Fig. 1 shows that pX penetrated all parts of the sample.

Evaluation of the  $T_g$  data and other features of the TP evidence is continuing. In passing, we note that no  $T_g$  for PB could be detected. This indicates that no microphase separation of the rubbery PB occurred, despite its intrinsic incompatibility with PMMA. Apparently the PB-crosslinking reaction succeeded in "locking" the PB chains irreversibly around the host PMMA network chains, preventing PB segregation. This sort of microscopic homogeneity is highly desirable, as phase separation would almost surely lead to inferior properties.

#### CONCLUSION

The final stages of this project (Ms. Stoughton's Ph.D. thesis research) are still in progress. Attached is the thesis Table of Contents. Our plan is to submit the thesis itself as the completed version of this Final Technical Report. All the mechanical property data, property correlations, and comparisons with theoretical models for predicting linear behavior, will be contained therein.

## REFERENCES

1. G. Akovali, K. Biliyar, and M. Shen, "Gradient Polymers by Diffusion Polymerization," J. Appl. Polym. Sci., 20, 2419 (1976).
2. C.F. Jasso, S.D. Hong, and M. Shen, "Stress-Strain Behavior of Some Acrylic Gradient Polymers," ACS Polym Preprints, 19(1), 63 (1978).
3. G.C. Martin, E. Enssani, and M. Shen, "The Mechanical Properties of Gradient Polymers," J. Appl. Polym. Sci., 26, 1465 (1981).

## Thesis Outline

Abstract

Table of Contents

### Chap. 1: Introduction

- A. Purpose of investigation. Review of gradient polymer literature and potential.
- B. Criteria for selection of preparative methods.
- C. Summary of tests conducted--MTS, TP, SEM/EDAX--and goals of each test.

### Chap. 2: Sample Preparation

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- B. Chemical reactions for PB.
- C. Apparatus for polymerizations.
- D. Experimental procedures.
- E. Extraction of soluble residue.

### Chap. 3: Sample Characterization (General)

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- B. Flory-Huggins parameters.
- C. Density.
- D. Para-xylene content.

### Chap. 4: Composition Profiles (SEM/EDAX)

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- D. Procedures for volumetric changes (at lowest strain rate).
- E. Procedures for slow cyclic strain and recovery.
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- B. Evaluation and tabulation of moduli ( $E$ ), yield points ( $\sigma_y, \epsilon_y$ ), fracture points ( $\sigma_f, \epsilon_f$ ), and toughness ( $w$ ).
- C. Correlations, with average sample compositions and with gradient type.
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- E. Comparisons of  $E$  and other parameters with model.
- F. Strain-rate fracture envelope.

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- B. Surface features - ductile and brittle fracture mechanisms and evidence.
- C. Correlation with crack propagation rates - flaw/void initiation, slow/stable crack growth, fast/stable crack propagation, fast/unstable crack growth.
- D. Comparison to literature on PMMA and rubber.

Chap. 8: Volume Dilation

- A. Computational methods.
- B. Data - volume vs. axial strain.
- C. Influence of sample composition.

Chap. 9: Slow Cyclic Tensile Tests

- A.  $\sigma(\epsilon)$  closed-loop curves for all samples.
- B. Evaluation and tabulation of E, yield point, permanent set, and hysteresis of each cycle, and ultimate fracture parameters.
- C. Data interpretation.

Chap. 10: Fatigue in Rapid Cycling

- A. Data.
- B. Interpretation - elastic and plastic strain, hysteresis, creep during testing.
- C. Correlations with compositional factors.

Chap. 11: Torsional Pendulum Testing

- A. Description of TP
- B. Modifications.
- C. Procedures and calibration.
- D. Results - shear moduli (storage modulus  $G'$  and loss modulus  $G''$ ) from  $-100^{\circ}\text{C}$  to  $+120^{\circ}\text{C}$ .
- E. Comparisons with literature on PMMA, PB, various IPN's, and various two-phase rubber-toughened plastics.
- F. Evidence for microscopic phase separation.
- G. Consistency with MTS data.

Chap. 12: Review and Conclusions

- A. Overall evaluation of all data.
- B. Implications for optimal design of gradient polymers.
- C. Recommendations for future work.

ReferencesAppendices

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